EMPIRICAL TUNING METHODOLOGY FOR As AND Cl DOPING OF MOCVD GROWN CdTe.

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Summary:

- CdTe-based photovoltaic solar cells tend to rely on $CdCl_2$ treatments, using conventional deposition techniques, to achieve high efficiencies.
- Metal Organic Chemical Vapour Deposition (MOCVD) is a deposition technique which enables a large number of growth parameters to be varied with a high repeatability, such as; the II:VI precursors ratios, the doping concentration, the layer thicknesses and the growth temperatures.
- All CdTe/CdS structures were grown by MOCVD onto commercial ITO/glass substrates. Arsenic concentration as high as 3 x 10^{18} atoms.cm^{-3} can be substituted into CdTe layers grown by MOCVD. Controlled Arsenic and Chlorine doping was studied as a potential alternative to $CdCl_2$ treatments.
- To avoid the investigation of a large number of growth runs, a strategic statistical approach, named Taguchi method, was used to setup and carry out a given set of growth experiments. The method allowed efficient identification of the parameters most beneficial to the characteristics of a photovoltaic solar cell.
- Our best solar cell efficiency to date is 6% ,without any $CdCl_2$ treatment, where the CdTe absorber, grown at 390°C, was Cd-rich and doped with As.

Growth of the CdTe/CdS Structure by MOCVD:

The CdTe/CdS structure was grown at atmospheric pressure, by MOCVD, under H_2, in a horizontal reactor. The as-grown layer thicknesses were monitored in real-time by a novel *in situ* triple wavelength interferometer. The metal organic precursors for Cd, Te and S were:

- Dimethylcadmium (**DMCd**),
- Diisopropyltelluride (**DIPTe**) and,
- Ditertiarybutylsulphide (**DTBS**) respectively.

For the *in situ* arsenic doping in the CdTe layers, Tris-Dimethylaminoarsine (**TDMAAs**) was used in a double dilution line arrangement (stable molar flow while keeping a low partial pressure).

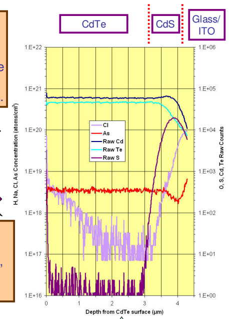
The n-Hexylchloride (**n-HexCl**) precursor was used in two ways:

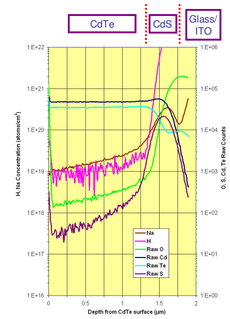
- As a direct *in situ* dopant, using only a 2 sccm flow in the line (10 sccm in CdS),
- As an *in situ* $CdCl_2$ post-growth treatment in an attempt to grow cap layer. The Cd:Cl precursor ratio was kept at 2.5.

The numerous growth and post-growth parameters studied are listed in the figure below. In brackets are the number of levels per parameters.

Arsenic concentration is constant throughout the CdTe layer, which is enhanced by an increase in point defects growing under Cd-rich conditions.

The *in situ* $CdCl_2$ treatment showed a gradual, time dependent, diffusion from the CdTe surface.





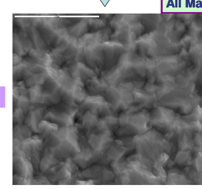
Impurities such as Na from the soda lime glass diffuse rapidly through the whole structure due to the annealing process.

Even the sulphur diffuses into the CdTe, having a dramatic effect on the interface and the overall cell performance.

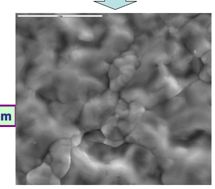
Varied Parameters | **MOCVD Process Steps** | **Conventional Combinations**

Varied Parameters	MOCVD Process Steps	Conventional Combinations
TCO coated Glass substrate (2)	SUPERSTRATE CONFIGURATION	2
• Thickness t_{CdS} (4), • II:VI ratio (3), • Temperature T_{sub} (3), • Cl doping (2), • Annealing (2), • Te buffer layer (2).	n-type CdS	288
• Thickness t_{CdTe} (3), • II:VI ratio (2), • Temperature T_{sub} (2), • As doping (4), • Cl doping (2).	p-type CdTe	96
• n-HexCl flow (2), • Time (2).	*In situ* $CdCl_2$ treatment	5
• Time (2), • Ambient gas (2).	*In situ* post-growth anneal	5

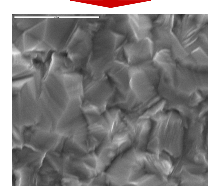
All Markers are 5µm



Surface morphology of a CdTe layer, grown by MOCVD, at 350°C.



Annealing the device at 500°C enhances the coalescence of adjacent grains. The CdTe surface appears smoother



By increasing T_{sub} to 390°C, the morphology changed with larger grains appearing to have a different crystal orientation.

Device preparation for J-V characterisation:

For the purpose of this study the back contacts were formed by Br/MeOH etch (0.25%) and evaporated Au contacts. 10 x 2.5 mm² Au dots were deposited on each sample to ensure consistency in the results throughout the sample's surface.

Some NP etched samples resulted in higher efficiency but the Br/MeOH was more consistent and therefore more suited to the Taguchi design of experiment.

Total combinations:
1,382,400

An alternative experimental method was needed: The Taguchi method.

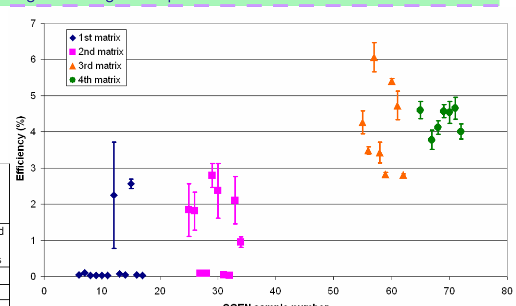
- 4 matrices which includes set of growth experiments were designed; one with 12 levels (L_{12}) and three with 8 levels (L_8).
- The number of growth experiments where then reduced from 1,382,400 to 36!
- The J-V characterisation of the grown devices allowed to explore and select the best parameters based on the usual solar cells performance (i.e. η, J_{sc}, V_{oc}, FF).
- The best device from one matrix was always carried to the following one to confirm its reproducibility.

Example using the cell efficiency analysis from the 3rd Taguchi matrix.

Run name	CdS T_{sub} (°C)	CdS II:VI	CdS T_{sub} / II:VI	t_{CdS} (nm)	t_{CdTe} (µm)	CdTe T_{sub} (°C)	As doping (partial pressure / x10^{-7} atm)	η(%)
	(-) : 300 (+): 330	(-) : 0.76 (+): 1		(-) : 240 (+): 350	(-) : 4 (+): 6	(-) : 350 (+): 390	(-) : 4 (+): 8	Averaged over 10 contacts
SGEN55	-	-	-	-	-	-	-	4.26
SGEN56	-	-	-	+	+	+	+	3.49
SGEN57	-	+	+	-	-	+	+	6.07
SGEN58	-	+	+	+	+	-	-	3.43
SGEN59	+	-	+	-	+	-	+	2.83
SGEN60	+	-	+	+	-	+	-	5.4
SGEN61	+	+	-	-	+	+	-	4.73
SGEN62	+	+	-	+	-	-	+	2.81
	-1.48	1.06	2.44	-2.76	-4.06	6.36	-2.62	

(-4.26-3.49-6.07-3.43+2.83+5.4+4.73+2.81) = -1.48

	Main parameter affecting the cells Efficiency	
Taguchi matrix	With a positive effect	With a negative effect
1	Arsenic doping	Long annealing 500°C
2	*in situ* $CdCl_2$ treatment	Short annealing 500°C
3	T_{sub} at 390°C during CdTe growth	t_{CdTe} increased to 6µm
4	T_{sub} at 315°C during CdS growth	Cl doping of CdS



The efficiency of the devices clearly improves from one matrix to the next. The divergence and scattering of the efficiency results reduce, which show the robustness of the Taguchi method and how it can improve device parameters.

The same analysis can easily be applied, using the Taguchi method, to analyse and fine tune other solar cells characteristics such as the V_{oc}, J_{sc} and FF.

Conclusion:

1. The efficiency increased from 0 to 6 % in only 36 growth experiments using the Taguchi method,
2. The Arsenic doping of the CdTe absorber was an important parameter for the J_{sc} and consequently for the η,
3. MOCVD technique is perfectly suited for tailoring II:VI devices and offers good process repeatability.

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